Book Reviews*

Tables of Resolving Agents and Optical Resolutions. By SAMUEL H. WILEN (City University of New York). University of Notre Dame Press, Notre Dame, Ind. 1972. 308 pp. $14.95.

The material tabulated in this useful book is the result of a staggering amount of dedicated labor, and chemists who must deal with optical resolutions will have many occasions to be grateful to the compiler. There are two major divisions: Resolving Agents (25 pp) and Resolutions (268 pp). The first of these lists in alphabetical order an amazing variety of agents, giving their specific rotation, commercial suppliers, and references. The second section lists resolutions of about 1200 organic compounds published between mid-1950 and mid-1971. For each resolution, the structure of the compound resolved, the resolving agent and solvent, the specific rotation of the resolved compound, and references are given. The arrangement is by formula index, but use is made easy by the fact that the section is subdivided according to class of compound (*e.g.*, carboxylic acids, heterocyclic amines, acyclic alcohols, etc.).

Although lists of resolutions have been published before, none have been so comprehensive or have given so much information. Those who have had to make searches for resolution methods know how difficult it is, for the abstracting and indexing journals customarily focus on compounds rather than methods. A single occasion of using this compendium is likely to pay for the price in labor saved (a subsidy has helped keep the cost low).

These tables are meant as a supplement to the compiler's chapter "Resolving Agents and Resolutions in Organic Chemistry," published in Volume 6 of "Topics in Stereochemistry," edited by Allinger and Eliel. Reprints of this chapter separately are offered at $5.00 (University of Notre Dame Press). Both it and the compendium should be considered essential in any library catering to organic research chemists.

Semiempirical Wave-mechanical Calculations on Polyatomic Molecules. By RAYMOND DAUDEL and CAMILLE SANDORFY. Yale University Press, New Haven, Conn. 1971. xiii + 133 pp. $10.00.

This was written by Daudel and Sandorfy to be a companion volume to "Sigma Molecular Orbital Theory" by Sinanoğlu and Wiberg; these two volumes, together with "Three Approaches to Electron Correlation in Atoms" by Sinanoğlu and Brueckner constitute a trilogy (all published by Yale University Press), surveying certain aspects of the field of nonempirical, semiempirical, and empirical quantum mechanical calculation methods and results for molecular systems of chemical interest. It is the stated intent of Daudel and Sandorfy to present the most important stages in the evolution of the σ- or all-valence-electron epoch in theoretical chemistry, up to the end of 1969. However, as they note in their preface an explosion of published results has prevented comment on every relevant paper, and we may justifiably anticipate that the end of the evolution of semiempirical calculations is not yet in sight.

The book is divided into four chapters titled Empirical Methods (22 pp), Semiempirical Methods (43 pp), Methods Based on Bond Orbitals and Polyelectronic Functions (25 pp), and Recent Developments (18 pp). The first chapter is devoted to a brief survey of the earlier Hückel-type calculations, including the "C" approximation (treating only C–C bonds of saturated and substituted hydrocarbons in a Hückel-type calculation), the "H" approximation (adding C–H bonding and overlap integrals to the Hückel matrix), and the extended Hückel method (including all-valence-electron bond integrals within the Hückel formulation). The second chapter (about twice as long as each of the other three) discusses adaptations of the Pariser–Parr–Pople π-electron method for σ-electron systems. The VESCF, CNDO, NDDO, INDO (a page of the preface is devoted to a glossary of some acronyms familiar to researchers in the semiempirical field), and various other neglect-of-differential-overlap approaches to SCF and CI results are reviewed here. The presentation in this chapter (as throughout the book) is in the form of a survey of published results, with little textbook development of equations or models; comparisons between the results of the various semiempirical methods are limited to those presented in the literature surveyed. Chapter 3 reviews the semiempirical methods which attempt to account for electron correlation using multielectron basis functions. Most of these emphasize the localized nature of the chemical bond, such as McWeeney's localized geminals, and Hall's bond orbitals, both of which are bridged by Daudel's localized two-electron bonds, called two-electron loges. Bratoz' nonlocalized biorbitals are also briefly referenced.

The last chapter contains a paragraph each on recent advances and results for each of the methods discussed in the previous three chapters plus a final paragraph devoted to related valence-bond calculations.

The development of the various semiempirical theories has not been very uniform, and this presentation reflects the discontinuities inherent in the various attempts to emphasize and explore some (hopefully the important) aspects of a complete theory while disregarding the remaining aspects. The problem is intensified by the attempt to reference 442 publications within the confines of 108 pages. This has resulted in many (sometimes rather loosely related) references being reduced to single sentences (overlooking the obvious truncation of a discussion of one of Joyce Kaufman's papers in the middle of a sentence on page 31 due to a typographical error). Thus Section 4 of Chapter 4, titled "Calculation on Individual Molecules," covers about one side of one page and references 24 separate works. This is understandably the most heavily referenced page in the book but illustrates a necessitated lack of comparative critical review in many places.

Although undoubtedly already out of date for the most recent advances in semiempirical calculations, this book serves well the function of a quick survey of the work up through 1969, and will introduce the interested reader to the more significant references appearing in the journal literature.

Don R. McLaughlin, *University of New Mexico*

Progress in Physical Organic Chemistry. Volume 9. Edited by A. STREITWIESER (University of California—Berkeley) and R. W. TAFT (University of California—Irvine). Wiley-Interscience, New York, N. Y. 1972. vii + 354 pp. $22.50.

This book represents another excellent contribution in an already excellent series; its high cost per page might discourage individuals, but it is a necessity for all institutional libraries. An excellent, concise, and entirely appropriate commemorative bibliography of the late Saul Winstein's work (written by A. S.) precedes the first chapter.

The first chapter, by M. R. Willcott, R. L. Cargill, and A. B. Sears, is on "Thermal Unimolecular Reactions." This is a tabulation of E_a and log A data, from 328 references, for such reactions. The purpose is to allow an experimental data cross-check on smooth, concerted, orbital-symmetry-"allowed" unimolecular reactions; such reactions should have activation energies substantially lower than the sum of the pertinent bond energies (and *vice versa* for stepwise, biradical symmetry-"forbidden" reactions). Grouping and confirming series of reactions of the same mechanistic type are also done by the magnitude of the log A values. The table is largely organized as to reactant structure class.

The second Chapter, "Semiempirical Molecular Orbital Calculations for Saturated Organic Molecules," by W. C. Herndon, begins with a general outline of the molecular orbital calculation problem, a discussion of the Hückel method, and simple LCAO methods (valence electron, etc.) for saturated systems. A substantial section on group and bond orbital approaches, with organization by pertinent related experimental physical parameters (ionization potentials, fragmentation, radiolysis, ΔH_f), follows. The final major section is a detailed description of the extended Hückel approach with a decidedly (and avowedly) negative summary as to the future of such an approach. The concluding remarks of Herndon's chapter relate the latter to recent increases in the number of applications of SCF treatments (316 references).

The chapter "Electrophilic Substitution at Alkanes and in Alkylcarbonium Ions," by D. M. Brouwer and H. Hogeveen, organizes 97 references (by the reaction classes below) in terms of rate constants, activation parameters, and some equilibrium data. These data were obtained largely by pmr (conventional reagent concentration change and line broadening) techniques in HF, HF–SbF_5, and other strong acid systems. There are two main categories: inter-

* Unsigned book reviews are by the Book Review Editor.

and intramolecular reactions. The intermolecular section is divided into carbonium ion processes by proton attack on C–H, C–D, and C–C bonds and by hydride and alkide transfer reactions. The summary discusses mechanistic and stereochemical implications. The intramolecular section is subdivided into alkide and hydride (1,2, 1,3, 1,4, and 1,5) shifts, rearrangements of alkyl carbonium ions (multistep, with and without branching changes), and protonated cyclopropane rings (in many systems).

The fourth chapter, "Proton Transfer in Highly Basic Media," by J. R. Jones, is essentially a review of work (149 references) in basic solutions to try to bring the recognition of the concepts up to that of acid-catalyzed reactions. The approach is essentially idea and concept development as contrasted to the data-tabulation approach of the preceding chapters. The format is defined in terms of weak acids (anions of measurable concentration, but not complete ionization), kinetic acidity, and the Brønsted relationship. Highly basic media (areas of applicability of basicity functions) are evolved as activity coefficient expressions, data reporting, and the interrelationship of the two. This is followed by isotope effects and labeling as related to base-catalysis mechanisms. This chapter seems to be more broadly and extensively developed than the corresponding chapter (Chapter 7) in Rochester's book: "Acidity Functions."

The final chapter, "Mechanistic Deductions from Solvent Isotope Effects," by R. L. Schowen, is introduced by a development of the effect in terms of bonding, labeling, and solvation changes during the reaction. Bonding energy is related to fractionation factors, and this is extrapolated to transition state conceptualized bonds. The theory and estimation of primary isotope effects are interrelated to justify an estimate of the complete solvent isotope effect involving transition states. The next section reverses the thought process to development of transition state "pictures" from solvent isotope effects for a number of reaction classes. The last section deals with solvent isotope effect results in the framework of well-investigated proton transfers in acid–base catalysis.

Terence C. Morrill, *Rochester Institute of Technology*

Fluoropolymers. Edited by L. A. Wall (National Bureau of Standards). Wiley-Interscience, New York, N. Y. 1972. x + 550 pp. $29.95.

This book, Volume XXV in the series "High Polymers," is a critical review of the available knowledge in the steadily growing field of fluorine-containing polymers. The book contains sixteen chapters written by fifteen different authors, of whom six are associated with the National Bureau of Standards. The first nine chapters deal with monomer synthesis and polymerization processes for a number of classes of fluoropolymers. The last seven chapters discuss crosslinking, thermal and radiation chemistry, surface properties, and structure *vs.* property relationships.

Generally, the chapters are well written with extensive bibliographies, and the book will be of value to those working in the area of fluoropolymers. The emphasis is on recent developments, mechanism studies, and the relationship of structure to chemical and physical behavior. There is very little information on polymer processing, mechanical properties, or applications, and the treatment of the preparations of the most commercially significant polymers is quite superficial. A more complete index would have facilitated the use of the book as a reference source.

David E. Rice, *3M Company*

Mechanical Properties of Solid Polymers. By I. M. Ward (University of Leeds). Wiley-Interscience, New York, N. Y. 1971. xv + 375 pp. $19.95.

This textbook on solid polymers is intended as an introductory course on the graduate level. It is readable by any engineer or scientist who has taken physics and mathematics through differential equations. Topics covered include finite strain elasticity, linear viscoelastic behavior, relaxation transitions, time–temperature equivalence, nonlinear viscoelastic behavior, anisotropic behavior, and yield and breaking phenomena.

The required mathematics, such as matrices used in finite strain elasticity, is covered in good detail. Experimental techniques are discussed in so far as they elucidate the property that is being measured. Molecular and structural interpretations are considered only after the phenomenological approach has been adequately treated. An extensive list of references is included at the end of each chapter.

This book should prove useful to many different groups of people: materials scientists who have not studied polymers, polymer chemists who have not been concerned with mechanical properties, engineers who have not studied viscoelastic materials, and many more. It is a very good introduction to the important area of the materials science of polymers in the solid state.

Geoffrey T. Fox, *University of Santa Clara*

Hydrogen Bonding. By Serge N. Vinogradov (Wayne State University) and Robert H. Linnell (University of Southern California). Van Nostrand Reinhold Co., New York, N. Y. 1971. xi + 319 pp. $9.50.

This book is intended to fill a need, perceived by its authors, for an elementary account of hydrogen bonding, intermediate in complexity and length between the discussions in textbooks and those in specialized monographs. It consists of ten chapters of roughly equal length. The first two, on chemical bonding and the physical properties of hydrogen-bonded systems, are of an introductory character, followed by three on experimental techniques and results (ir and Raman spectroscopy; nmr and uv spectroscopy; thermodynamics) and a chapter on models and theory. There is a chapter devoted to solids, one to biological materials and one on water, ice and aqueous solutions. A final, special-topics chapter treats conformational problems, reaction rates, and prototropic tautomerism. Each chapter has a list of "the leading references through 1968 and including some from 1969 and 1970." There are about 380 references in all; no author index is provided. Appendices contain tables of physical constants and logarithms and a collection of twenty problems with solutions. The problems universally involve the numerical calculation of equilibrium constants from experimental data.

The tenor of the book is introductory and elementary throughout. For example, explanations of such topics as molecular vibrations and nmr spectroscopy are given at the appropriate points. No subject is treated in depth, but the references should lead the interested reader to whatever level of sophistication he wants. "Hydrogen Bonding" may find use as a text for independent or interterm tutorial study by beginning students. A paperback version at lower cost would doubtless increase its attractiveness as a supplementary text in beginning chemistry courses and in the biological sciences.

Richard L. Schowen, *University of Kansas*

Comprehensive Analytical Chemistry. Volume IIC. Electrical Methods; Physical Separation Methods. Edited by C. L. Wilson (The Queen's University of Belfast) and D. W. Wilson (City of London Polytechnic). American Elsevier, New York, N. Y. 1971. xvi + 420 pp. $31.50.

This volume is composed of four chapters: Paper Chromatography and Thin-Layer Chromatography, by J. W. C. Peereboom (129 pp, 466 ref); Radiochemical Methods of Analysis, by D. Gibbons and D. A. Lambie (76 pp, 247 ref); Nuclear Magnetic Resonance and Electron Spin Resonance Methods, by B. D. Flockhart (112 pp, 170 ref); and X-Ray Spectrometry, by G. L. Macdonald (82 pp, 199 ref), in addition to a detailed index (21 pp). Each chapter begins with basic principles and develops the theory in a descriptive, rather than mathematical fashion. The sections on Experimental Apparatus and Analytical Applications will in many cases allow direct utilization of the technique. However, the coverage is generally not as exhaustive as that found in the much larger series edited by Kolthoff and Elving (*cf. Anal. Chem.*, 44 (6), 66A (1972)).

George H. Wahl, Jr., *North Carolina State University*

Search for New Drugs. Edited by Alan A. Rubin. Marcel Dekker, Inc., New York, N. Y. 1972. 452 pp. $19.50.

This book is sixth in a series of monographs on medicinal research and consists of nine chapters written by well-known researchers in clinically important areas where the ever elusive chase for superior drugs is being actively pursued. The first section deals with familiar fields of anti-inflammatory, anti-ulcer, and psychoactive drugs. Subsequent chapters discuss areas of selective beta-adrenergic receptor drug interaction, atherosclerosis, the interferon system, the origin and treatment of thrombosis, and the nascent fields of aging and memory.

The book succeeds in bringing to focus the deficiencies of the currently employed methodology in the evaluation of new drug promise for diseases which are etiologically least understood. The main theme of seeking cure by gaining fundamental causative knowledge instead of treating symptoms is dramatically put forth. Although the critical and authoritative treatment of classical therapy is excellent, the coverage in certain chapters of more recent therapeutic developments appears to be sketchy at best and some important pharmacological references have been omitted. Nevertheless,

clinical investigators will appreciate clear delineation of clinically established differences in a particular area and the brief summation of the effects of biological and synthetic medicinals.

The book should make provocative reading for pharmacologists and biologists and should also be of use to the medicinal chemists.

O. P. Goel, *Parke, Davis & Company*

Ions and Ion Pairs in Organic Chemistry. Volume I. Edited by MICHAEL SZWARC (State University College of Forestry, Syracuse). John Wiley and Sons, New York, N. Y. 1972. vii + 399 pp. $17.95.

The task of reviewing this distinctive and important volume has been accomplished most admirably by the Editor himself in his Preface to the volume, in which he provides a succinct but illuminating account of the background of the subject and outlines the general scope of the volume as well as the themes and significance of the individual chapters.

An introductory chapter, also by the Editor, elaborates the concept of ion pairs and discusses the nature and characteristic properties of the various different types of ion pairs and aggregates whose existence in solution can be recognized and distinguished. The chapter by P. Kebarle on "Ions and Ion-Solvent Molecule Interactions in the Gas Phase" is largely an account of work originating from the author's own laboratory, employing the elegant approaches and techniques for whose development he has been largely responsible. This is the most comprehensive account of this important subject of which this reviewer is aware and will be of considerable interest to inorganic and physical, as well as organic, chemists. J. Smid's chapter on "Spectrophotometric Studies of Ion-Pair Equilibria" is a thorough, critical, and scholarly account which encompasses a careful analysis of many data from the author's own as well as other laboratories and which emphasizes the limitations as well as applications of spectral studies (*e.g.*, the insensitivity of spectra of "loose" ion pairs to interionic distances and other structural parameters). The authoritative chapter by W. F. Edgell on "Infrared and Raman Studies of Ions and Ion Pairs" constitutes the only general account of this subject of which this reviewer is aware. Although this theme is not explicitly dealt with, the material in this chapter is relevant to an understanding of the marked effect of cations on the *reactivities* of anionic metal carbonyls and will, accordingly, be of interest to those concerned with this active field of research.

The remaining chapters deal with the applications of magnetic resonance to the study of ion pairs. The chapter by J. H. Sharp and M. C. R. Symons is a very clear, comprehensive, and readable account of electron spin resonance which, according to the authors, has "in recent years shed more light on the subject of ion pair formation . . . than any other physical or chemical technique." Two brief chapters by L. D. McKeever and by E. de Boer and J. L. Sommerdijk describe the specific applications of nuclear magnetic resonance to organolithium compounds and to alkali radical ion pairs, respectively. These are supplemented with an Appendix by the Editor describing additional applications of nuclear magnetic resonance such as the determination of solvation numbers of ions. The final chapter, by J. L. Sommerdijk and E. de Boer, discusses the quantitative aspects of electron spin and nuclear magnetic resonance studies of ion pairs and treats certain more complex aspects of ion-pair behavior such as intramolecular and intermolecular cation exchange and cation oscillations.

This reviewer shares the enthusiastic sentiment expressed in the last sentence of the Editor's Preface, *i.e.*, "In conclusion, the material presented in this volume not only demonstrates the existence of ion pairs but endows them with spirit of life and motion." This is an excellent, timely, and important book that will be of interest and value to chemists in a wide range of fields.

J. Halpern, *University of Chicago*

The Analytical Chemistry of Sulfur and Its Compounds. Part II. Edited by J. H. KARCHMER (Esso Research and Engineering Co.). Wiley-Interscience, New York, N. Y. 1972. xvi + 835 pp. $45.00.

This book is the second part of a three-part treatise on sulfur chemistry constituting Volume 29 in "Chemical Analysis." This volume treats sulfides, di- and polysulfides, thiophenes, sulfur analogs of carbonyls, carboxylic and carbonic acids, and tetra- and hexavalent sulfur compounds. Each chapter follows essentially the same format, discussing background chemistry, occurrence, physical properties and measurements, analytically significant chemical and physical properties, interfering materials, and recommended procedures for analysis of each of the families of compounds.

As in any review of this type, it is impossible to effect complete coverage of all the literature. However, where the authors do not or cannot go into more detail on specific procedures or type of compounds, or if the material has been reviewed before, many references are given to the original papers or review, making the literature searches of the workers in this field easier. Some of the references are as late as 1969. On the other hand, many of the better and recommended procedures for analysis are described in full detail, eliminating the need for further literature work.

Perhaps there are two minor drawbacks to this volume. The chapter on thiols was included in Part I when it seems more appropriate to have included it in this volume with the other organosulfur compounds (Part I is principally on inorganic sulfur compounds). Also, very little discussion is allotted to the nuclear magnetic resonance characteristics of these sulfur compounds in this volume, since this is the sole topic of Part III. This may necessitate the purchase of two volumes instead of one.

This book should prove very useful in reference and research libraries, as well as the personal libraries of researches in the field of sulfur chemistry.

Dwight W. Chasar, *Johnstown Campus, University of Pittsburgh*

Basic Chemistry. By WILLIAM S. SEESE (Casper College) and GUIDO H. DAUB (University of New Mexico). Prentice-Hall, Inc., Englewood Cliffs, N. J. 1972. 552 pp. $11.95.

"Basic Chemistry" is an easy textbook for first-course chemistry students who have not had any chemistry and have no great aptitude for science. This book is devoted almost exclusively to physical chemistry, and the usual sequence of subjects is used.

"Basic Chemistry" is reasonably well written, has many lucid illustrations, explains chemistry quite well, and tells several interesting stories. The factor method for calculations is used and is well illustrated in the text. A number of rather easy problems are provided for each chapter, along with some answers. The subjects which are covered in this text are well covered in a simplified manner. For example, activation energy is not mentioned in the book.

"Basic Chemistry" covers atomic structure, equations, stoichiometry, and physical chemistry quite well. Not considered are analytical chemistry (except normality and titration), inorganic chemistry (except a few structures), organic chemistry, or natural products. For a well-balanced, first course in chemistry, these subjects should be included. In my opinion, this book is much too limited in scope to be a useful textbook for beginning students.

Alan Roebuck, *Purdue University, Calumet Campus*